A Chromium Diphosphine System for Catalytic Ethylene Trimerization: Synthetic and Structural Studies of Chromium Complexes with a Nitrogen-Bridged Diphosphine Ligand with *ortho*-Methoxyaryl Substituents

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Supporting Information
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Table 1. Crystal data and structure refinement for 16 (CCDC 187372).

Empirical formula	$C_{33}H_{31}NO_8P_2Cr \bullet C_4H_8O$
Formula weight	755.63
Crystallization Solvent	Tetrahydrofuran
Crystal Habit	Column
Crystal size	0.22 x 0.17 x 0.15 mm^3
Crystal color	Pale yellow

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 22989 reflections used in lattice determination	2.17 to 28.83°
Unit cell dimensions	a = 11.7105(5) Å b = 16.3059(8) Å β= 102.3330(10)° c = 19.3321(9) Å
Volume	3606.3(3) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.392 Mg/m^3
F(000)	1576
Data collection program	Bruker SMART v5.054
θ range for data collection	1.65 to 28.43°
Completeness to θ = 28.43°	95.2 %
Index ranges	$-15 \le h \le 15$, $-21 \le k \le 21$, $-25 \le l \le 25$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	73667
Independent reflections	8644 [R_{int}= 0.0710]
Absorption coefficient	0.462 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9340 and 0.9053

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8644 / 0 / 585
Treatment of hydrogen atoms	Unrestrained, except for solvent
Goodness-of-fit on F^2	1.755
Final R indices [I>2σ(I), 6299 reflections]	R1 = 0.0394, *w*R2 = 0.0620
R indices (all data)	R1 = 0.0638, *w*R2 = 0.0642
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$

Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.585 and -0.470 e.Å^{-3}

Special Refinement Details

The crystals contain disordered THF solvent molecules cocrystallized with the species of interest. It was possible to obtain and refine a satisfactory model for the THF molecules using anisotropic displacement parameters for the heavy atoms and riding parameters for the hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters and all non-solvent hydrogen atoms were refined without restraint.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 16. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cr(1)	499(1)	8615(1)	2467(1)	14(1)
P(1)	389(1)	10012(1)	2150(1)	13(1)
P(2)	1902(1)	9423(1)	3240(1)	14(1)
O(1)	-1340(1)	8849(1)	3329(1)	32(1)
O(2)	-1436(1)	7866(1)	1383(1)	26(1)
O(3)	1947(1)	8082(1)	1423(1)	27(1)
O(4)	1000(1)	6963(1)	3159(1)	28(1)
O(5)	-2105(1)	9720(1)	1502(1)	23(1)
O(6)	2576(1)	9868(1)	1637(1)	18(1)
O(7)	3913(1)	10476(1)	4000(1)	24(1)
O(8)	2293(1)	8213(1)	4276(1)	28(1)
N	1503(1)	10324(1)	2809(1)	13(1)
C(1)	-611(2)	8787(1)	3018(1)	18(1)
C(2)	-693(2)	8177(1)	1798(1)	18(1)
C(3)	1448(2)	8331(1)	1833(1)	19(1)
C(4)	834(2)	7608(1)	2904(1)	19(1)
C(5)	-3237(2)	9354(2)	1257(2)	35(1)
C(6)	3699(2)	9729(2)	1483(1)	27(1)
C(7)	4744(2)	11076(2)	4332(1)	36(1)
C(8)	2650(3)	7500(2)	4687(2)	51(1)
C(9)	2164(2)	11093(1)	2806(1)	19(1)
C(10)	-878(2)	10607(1)	2276(1)	14(1)
C(11)	-2022(2)	10350(1)	1975(1)	18(1)
C(12)	-2977(2)	10734(1)	2149(1)	22(1)

C(13)	-2816(2)	11399(1)	2602(1)	24(1)
C(14)	-1705(2)	11676(1)	2891(1)	21(1)
C(15)	-744(2)	11275(1)	2738(1)	18(1)
C(16)	688(2)	10424(1)	1332(1)	14(1)
C(17)	1747(2)	10241(1)	1133(1)	16(1)
C(18)	1903(2)	10435(1)	462(1)	20(1)
C(19)	1024(2)	10834(1)	-11(1)	22(1)
C(20)	9(2)	11064(1)	187(1)	21(1)
C(21)	-154(2)	10854(1)	855(1)	19(1)
C(22)	3468(2)	9261(1)	3344(1)	17(1)
C(23)	4316(2)	9800(1)	3717(1)	22(1)
C(24)	5499(2)	9618(2)	3790(1)	33(1)
C(25)	5833(2)	8903(2)	3518(1)	39(1)
C(26)	5020(2)	8352(2)	3174(1)	35(1)
C(27)	3844(2)	8535(1)	3088(1)	25(1)
C(28)	1764(2)	9578(1)	4149(1)	14(1)
C(29)	1994(2)	8897(1)	4599(1)	18(1)
C(30)	1916(2)	8949(1)	5301(1)	22(1)
C(31)	1594(2)	9683(1)	5559(1)	22(1)
C(32)	1347(2)	10356(1)	5122(1)	21(1)
C(33)	1431(2)	10301(1)	4420(1)	17(1)
O(41)	5099(2)	1762(1)	-329(1)	55(1)
C(42A)	5341(6)	1959(8)	461(4)	40(3)
C(42B)	5694(8)	1476(5)	352(3)	62(2)
C(43)	6610(2)	2081(2)	625(1)	51(1)
C(44)	6927(2)	2401(1)	-32(1)	37(1)
C(45)	5771(2)	2389(1)	-559(1)	34(1)

Table 3. Selected bond lengths [Å] and angles [°] for 16.

Cr(1)-C(2)	1.8328(19)	C(4)-Cr(1)-C(3)	89.00(8)
Cr(1)-C(4)	1.850(2)	C(1)-Cr(1)-C(3)	171.30(8)
Cr(1)-C(1)	1.870(2)	C(2)-Cr(1)-P(1)	101.66(6)
Cr(1)-C(3)	1.879(2)	C(4)-Cr(1)-P(1)	166.30(6)
Cr(1)-P(1)	2.3557(6)	C(1)-Cr(1)-P(1)	89.79(6)
Cr(1)-P(2)	2.3712(5)	C(3)-Cr(1)-P(1)	94.37(6)
		C(2)-Cr(1)-P(2)	169.10(6)
C(2)-Cr(1)-C(4)	91.85(8)	C(4)-Cr(1)-P(2)	98.90(6)
C(2)-Cr(1)-C(1)	86.74(8)	C(1)-Cr(1)-P(2)	91.68(6)
C(4)-Cr(1)-C(1)	88.73(8)	C(3)-Cr(1)-P(2)	96.97(6)
C(2)-Cr(1)-C(3)	84.94(8)	P(1)-Cr(1)-P(2)	67.536(18)
O(1)-C(1)	1.150(2)	O(4)-C(4)-Cr(1)	177.00(17)
O(2)-C(2)	1.166(2)		
O(3)-C(3)	1.154(2)		
O(4)-C(4)	1.161(2)		
O(1)-C(1)-Cr(1)	175.11(16)		
O(2)-C(2)-Cr(1)	177.11(16)		
O(3)-C(3)-Cr(1)	172.19(16)		

Table 4. Bond lengths [Å] and angles [°] for 16.

Cr(1)-C(2)	1.8328(19)	C(15)-H(15)	1.017(15)
Cr(1)-C(4)	1.850(2)	C(16)-C(21)	1.388(2)
Cr(1)-C(1)	1.870(2)	C(16)-C(17)	1.407(2)
Cr(1)-C(3)	1.879(2)	C(17)-C(18)	1.384(2)
Cr(1)-P(1)	2.3557(6)	C(18)-C(19)	1.385(3)
Cr(1)-P(2)	2.3712(5)	C(18)-H(18)	0.967(17)
P(1)-N	1.6946(14)	C(19)-C(20)	1.376(3)
P(1)-C(16)	1.8206(17)	C(19)-H(19)	0.947(16)
P(1)-C(10)	1.8321(18)	C(20)-C(21)	1.388(2)
P(1)-P(2)	2.6274(7)	C(20)-H(20)	0.927(17)
P(2)-N	1.7046(14)	C(21)-H(21)	0.932(16)
P(2)-C(28)	1.8168(17)	C(22)-C(27)	1.390(3)
P(2)-C(22)	1.8211(18)	C(22)-C(23)	1.405(2)
O(1)-C(1)	1.150(2)	C(23)-C(24)	1.394(3)
O(2)-C(2)	1.166(2)	C(24)-C(25)	1.371(3)
O(3)-C(3)	1.154(2)	C(24)-H(24)	0.859(18)
O(4)-C(4)	1.161(2)	C(25)-C(26)	1.373(3)
O(5)-C(11)	1.364(2)	C(25)-H(25)	0.88(2)
O(5)-C(5)	1.437(2)	C(26)-C(27)	1.384(3)
O(6)-C(17)	1.363(2)	C(26)-H(26)	0.890(19)
O(6)-C(6)	1.427(2)	C(27)-H(27)	0.954(16)
O(7)-C(23)	1.358(2)	C(28)-C(33)	1.380(2)
O(7)-C(7)	1.433(2)	C(28)-C(29)	1.400(2)
O(8)-C(29)	1.359(2)	C(29)-C(30)	1.383(2)
O(8)-C(8)	1.420(3)	C(30)-C(31)	1.379(3)
N-C(9)	1.473(2)	C(30)-H(30)	0.923(17)
C(5)-H(5A)	1.07(2)	C(31)-C(32)	1.377(3)
C(5)-H(5B)	1.01(2)	C(31)-H(31)	0.951(16)
C(5)-H(5C)	0.95(2)	C(32)-C(33)	1.385(2)
C(6)-H(6A)	0.973(19)	C(32)-H(32)	0.904(17)
C(6)-H(6B)	0.97(2)	C(33)-H(33)	0.958(16)
C(6)-H(6C)	0.94(2)	O(41)-C(45)	1.419(2)
C(7)-H(7A)	0.95(2)	O(41)-C(42B)	1.431(6)
C(7)-H(7B)	1.013(19)	O(41)-C(42A)	1.527(9)
C(7)-H(7C)	0.98(2)	C(42A)-C(43)	1.465(7)
C(8)-H(8A)	0.90(2)	C(42A)-H(42A)	0.9900
C(8)-H(8B)	1.02(2)	C(42A)-H(42B)	0.9900
C(8)-H(8C)	0.98(2)	C(42B)-C(43)	1.469(5)
C(9)-H(9A)	0.961(16)	C(42B)-H(42C)	0.9900
C(9)-H(9B)	1.032(18)	C(42B)-H(42D)	0.9900
C(9)-H(9C)	0.968(18)	C(43)-C(44)	1.492(3)
C(10)-C(15)	1.396(2)	C(43)-H(43A)	0.9900
C(10)-C(11)	1.405(2)	C(43)-H(43B)	0.9900
C(11)-C(12)	1.386(3)	C(43)-H(43C)	0.9900
C(12)-C(13)	1.381(3)	C(43)-H(43D)	0.9900
C(12)-H(12)	0.909(18)	C(44)-C(45)	1.511(3)
C(13)-C(14)	1.377(3)	C(44)-H(44A)	0.9900
C(13)-H(13)	0.914(18)	C(44)-H(44B)	0.9900
C(14)-C(15)	1.387(3)	C(45)-H(45A)	0.9900
C(14)-H(14)	0.905(18)	C(45)-H(45B)	0.9900

C(2)-Cr(1)-C(4)	91.85(8)
C(2)-Cr(1)-C(1)	86.74(8)
C(4)-Cr(1)-C(1)	88.73(8)
C(2)-Cr(1)-C(3)	84.94(8)
C(4)-Cr(1)-C(3)	89.00(8)
C(1)-Cr(1)-C(3)	171.30(8)
C(2)-Cr(1)-P(1)	101.66(6)
C(4)-Cr(1)-P(1)	166.30(6)
C(1)-Cr(1)-P(1)	89.79(6)
C(3)-Cr(1)-P(1)	94.37(6)
C(2)-Cr(1)-P(2)	169.10(6)
C(4)-Cr(1)-P(2)	98.90(6)
C(1)-Cr(1)-P(2)	91.68(6)
C(3)-Cr(1)-P(2)	96.97(6)
P(1)-Cr(1)-P(2)	67.536(18)
N-P(1)-C(16)	106.32(8)
N-P(1)-C(10)	104.87(8)
C(16)-P(1)-C(10)	103.41(8)
N-P(1)-Cr(1)	96.03(5)
C(16)-P(1)-Cr(1)	124.92(6)
C(10)-P(1)-Cr(1)	118.62(6)
N-P(1)-P(2)	39.52(5)
C(16)-P(1)-P(2)	127.54(6)
C(10)-P(1)-P(2)	120.90(6)
Cr(1)-P(1)-P(2)	56.514(16)
N-P(2)-C(28)	106.41(8)
N-P(2)-C(22)	110.09(8)
C(28)-P(2)-C(22)	102.03(8)
N-P(2)-Cr(1)	95.19(5)
C(28)-P(2)-Cr(1)	119.64(6)
C(22)-P(2)-Cr(1)	122.30(6)
N-P(2)-P(1)	39.24(5)
C(28)-P(2)-P(1)	122.76(6)
C(22)-P(2)-P(1)	129.24(6)
Cr(1)-P(2)-P(1)	55.950(16)
C(11)-O(5)-C(5)	117.53(16)
C(17)-O(6)-C(6)	117.89(15)
C(23)-O(7)-C(7)	118.25(17)
C(29)-O(8)-C(8)	119.26(17)
C(9)-N-P(1)	125.05(12)
C(9)-N-P(2)	130.18(13)
P(1)-N-P(2)	101.24(7)
O(1)-C(1)-Cr(1)	175.11(16)
O(2)-C(2)-Cr(1)	177.11(16)
O(3)-C(3)-Cr(1)	172.19(16)
O(4)-C(4)-Cr(1)	177.00(17)
O(5)-C(5)-H(5A)	111.3(11)
O(5)-C(5)-H(5B)	110.1(12)
H(5A)-C(5)-H(5B)	109.5(17)
O(5)-C(5)-H(5C)	108.0(13)
H(5A)-C(5)-H(5C)	108.0(17)
H(5B)-C(5)-H(5C)	109.9(17)
O(6)-C(6)-H(6A)	104.3(11)
O(6)-C(6)-H(6B)	110.7(12)
H(6A)-C(6)-H(6B)	107.5(16)
O(6)-C(6)-H(6C)	108.3(12)
H(6A)-C(6)-H(6C)	115.2(17)
H(6B)-C(6)-H(6C)	110.6(16)
O(7)-C(7)-H(7A)	107.6(13)
O(7)-C(7)-H(7B)	109.7(11)
H(7A)-C(7)-H(7B)	105.6(17)
O(7)-C(7)-H(7C)	110.4(13)
H(7A)-C(7)-H(7C)	116.0(18)
H(7B)-C(7)-H(7C)	107.3(16)
O(8)-C(8)-H(8A)	106.2(15)
O(8)-C(8)-H(8B)	106.4(13)
H(8A)-C(8)-H(8B)	103(2)
O(8)-C(8)-H(8C)	112.4(14)
H(8A)-C(8)-H(8C)	114(2)
H(8B)-C(8)-H(8C)	113.4(18)
N-C(9)-H(9A)	111.0(10)
N-C(9)-H(9B)	107.6(10)
H(9A)-C(9)-H(9B)	110.3(14)
N-C(9)-H(9C)	111.5(10)
H(9A)-C(9)-H(9C)	106.7(14)
H(9B)-C(9)-H(9C)	109.8(14)
C(15)-C(10)-C(11)	117.78(17)
C(15)-C(10)-P(1)	120.95(14)
C(11)-C(10)-P(1)	120.89(14)
O(5)-C(11)-C(12)	123.88(17)
O(5)-C(11)-C(10)	115.39(16)
C(12)-C(11)-C(10)	120.72(17)
C(13)-C(12)-C(11)	120.10(19)
C(13)-C(12)-H(12)	118.4(12)
C(11)-C(12)-H(12)	121.5(11)
C(14)-C(13)-C(12)	120.25(19)
C(14)-C(13)-H(13)	121.8(11)
C(12)-C(13)-H(13)	117.9(11)
C(13)-C(14)-C(15)	119.89(19)
C(13)-C(14)-H(14)	120.3(12)
C(15)-C(14)-H(14)	119.9(12)
C(14)-C(15)-C(10)	121.20(19)
C(14)-C(15)-H(15)	116.4(8)
C(10)-C(15)-H(15)	122.3(8)
C(21)-C(16)-C(17)	117.91(16)
C(21)-C(16)-P(1)	121.51(14)
C(17)-C(16)-P(1)	120.27(13)
O(6)-C(17)-C(18)	123.76(17)
O(6)-C(17)-C(16)	115.70(15)
C(18)-C(17)-C(16)	120.54(17)
C(17)-C(18)-C(19)	119.86(19)
C(17)-C(18)-H(18)	119.5(10)
C(19)-C(18)-H(18)	120.6(10)

C(20)-C(19)-C(18)	120.60(19)	C(42B)-O(41)-C(42A)	36.6(3)
C(20)-C(19)-H(19)	119.0(11)	C(43)-C(42A)-O(41)	102.0(5)
C(18)-C(19)-H(19)	120.3(11)	C(43)-C(42A)-H(42A)	111.4
C(19)-C(20)-C(21)	119.34(19)	O(41)-C(42A)-H(42A)	111.4
C(19)-C(20)-H(20)	121.6(10)	C(43)-C(42A)-H(42B)	111.4
C(21)-C(20)-H(20)	119.1(11)	O(41)-C(42A)-H(42B)	111.4
C(20)-C(21)-C(16)	121.57(19)	H(42A)-C(42A)-H(42B)	109.2
C(20)-C(21)-H(21)	118.2(10)	O(41)-C(42B)-C(43)	106.7(4)
C(16)-C(21)-H(21)	120.2(10)	O(41)-C(42B)-H(42C)	110.4
C(27)-C(22)-C(23)	118.19(17)	C(43)-C(42B)-H(42C)	110.4
C(27)-C(22)-P(2)	118.20(15)	O(41)-C(42B)-H(42D)	110.4
C(23)-C(22)-P(2)	123.42(14)	C(43)-C(42B)-H(42D)	110.4
O(7)-C(23)-C(24)	123.69(19)	H(42C)-C(42B)-H(42D)	108.6
O(7)-C(23)-C(22)	116.47(17)	C(42A)-C(43)-C(42B)	37.1(3)
C(24)-C(23)-C(22)	119.83(19)	C(42A)-C(43)-C(44)	106.8(3)
C(25)-C(24)-C(23)	120.1(2)	C(42B)-C(43)-C(44)	103.0(3)
C(25)-C(24)-H(24)	122.9(13)	C(42A)-C(43)-H(43A)	110.4
C(23)-C(24)-H(24)	117.0(13)	C(42B)-C(43)-H(43A)	77.9
C(24)-C(25)-C(26)	121.2(2)	C(44)-C(43)-H(43A)	110.4
C(24)-C(25)-H(25)	119.5(13)	C(42A)-C(43)-H(43B)	110.4
C(26)-C(25)-H(25)	119.2(13)	C(42B)-C(43)-H(43B)	140.3
C(25)-C(26)-C(27)	119.1(2)	C(44)-C(43)-H(43B)	110.4
C(25)-C(26)-H(26)	122.0(13)	H(43A)-C(43)-H(43B)	108.6
C(27)-C(26)-H(26)	118.9(13)	C(42A)-C(43)-H(43C)	136.0
C(26)-C(27)-C(22)	121.6(2)	C(42B)-C(43)-H(43C)	111.2
C(26)-C(27)-H(27)	120.9(10)	C(44)-C(43)-H(43C)	111.2
C(22)-C(27)-H(27)	117.5(10)	H(43A)-C(43)-H(43C)	34.9
C(33)-C(28)-C(29)	118.33(16)	H(43B)-C(43)-H(43C)	76.3
C(33)-C(28)-P(2)	125.16(14)	C(42A)-C(43)-H(43D)	75.8
C(29)-C(28)-P(2)	116.50(14)	C(42B)-C(43)-H(43D)	111.2
O(8)-C(29)-C(30)	125.33(17)	C(44)-C(43)-H(43D)	111.2
O(8)-C(29)-C(28)	113.54(16)	H(43A)-C(43)-H(43D)	133.7
C(30)-C(29)-C(28)	121.13(18)	H(43B)-C(43)-H(43D)	36.5
C(31)-C(30)-C(29)	119.23(19)	H(43C)-C(43)-H(43D)	109.1
C(31)-C(30)-H(30)	121.8(11)	C(43)-C(44)-C(45)	102.68(18)
C(29)-C(30)-H(30)	118.9(11)	C(43)-C(44)-H(44A)	111.2
C(32)-C(31)-C(30)	120.54(19)	C(45)-C(44)-H(44A)	111.2
C(32)-C(31)-H(31)	119.1(10)	C(43)-C(44)-H(44B)	111.2
C(30)-C(31)-H(31)	120.3(10)	C(45)-C(44)-H(44B)	111.2
C(31)-C(32)-C(33)	119.9(2)	H(44A)-C(44)-H(44B)	109.1
C(31)-C(32)-H(32)	120.5(11)	O(41)-C(45)-C(44)	106.00(17)
C(33)-C(32)-H(32)	119.6(11)	O(41)-C(45)-H(45A)	110.5
C(28)-C(33)-C(32)	120.82(18)	C(44)-C(45)-H(45A)	110.5
C(28)-C(33)-H(33)	119.9(10)	O(41)-C(45)-H(45B)	110.5
C(32)-C(33)-H(33)	119.3(10)	C(44)-C(45)-H(45B)	110.5
C(45)-O(41)-C(42B)	109.2(3)	H(45A)-C(45)-H(45B)	108.7
C(45)-O(41)-C(42A)	99.5(4)		

Table 5. Anisotropic displacement parameters ($Å^2 x 10^4$) for 16. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr(1)	149(2)	140(2)	128(2)	-5(1)	37(1)	-8(1)
P(1)	119(2)	151(3)	119(2)	1(2)	21(2)	-3(2)
P(2)	125(3)	144(3)	139(2)	6(2)	23(2)	8(2)
O(1)	259(9)	441(10)	303(8)	-62(7)	170(7)	-47(7)
O(2)	325(9)	253(8)	174(7)	0(6)	-11(7)	-109(7)
O(3)	317(9)	277(8)	272(8)	-44(7)	161(7)	19(7)
O(4)	389(9)	177(8)	273(8)	39(6)	75(7)	26(7)
O(5)	137(7)	283(8)	271(8)	-105(6)	17(6)	-27(6)
O(6)	146(7)	233(8)	193(7)	34(6)	78(6)	30(6)
O(7)	159(7)	251(8)	290(8)	-67(6)	7(6)	-41(6)
O(8)	453(10)	172(8)	188(7)	52(6)	5(7)	90(7)
N	116(8)	129(8)	125(8)	1(6)	4(6)	-29(6)
C(1)	197(11)	180(11)	138(10)	-13(8)	3(8)	-19(8)
C(2)	237(11)	158(10)	147(10)	32(8)	79(9)	-8(9)
C(3)	195(11)	155(10)	201(10)	13(8)	32(9)	-18(8)
C(4)	198(11)	219(11)	147(10)	-18(9)	55(8)	-17(9)
C(5)	173(12)	384(15)	468(16)	-175(13)	13(12)	-62(11)
C(6)	211(12)	316(14)	323(14)	66(12)	139(11)	46(11)
C(7)	278(14)	352(15)	416(16)	-98(13)	-2(12)	-98(12)
C(8)	930(30)	180(14)	308(15)	39(12)	-148(17)	123(15)
C(9)	202(12)	184(11)	190(11)	-7(9)	36(9)	-48(9)
C(10)	159(10)	140(10)	118(9)	33(8)	38(8)	28(8)
C(11)	196(11)	175(11)	170(10)	-7(8)	50(8)	4(8)
C(12)	128(11)	299(13)	221(11)	-8(9)	26(9)	13(9)
C(13)	211(12)	288(12)	234(11)	27(10)	91(9)	118(10)
C(14)	304(13)	167(11)	181(11)	-14(9)	70(9)	55(9)
C(15)	210(11)	175(11)	146(10)	29(8)	36(8)	12(9)
C(16)	165(10)	131(10)	121(9)	-12(8)	25(8)	-26(8)
C(17)	179(11)	129(10)	161(10)	-12(8)	18(8)	-30(8)
C(18)	221(12)	180(11)	217(11)	-28(9)	92(9)	-67(9)
C(19)	320(13)	211(12)	135(10)	8(9)	66(9)	-95(9)
C(20)	246(12)	205(11)	155(10)	49(9)	-17(9)	-33(9)
C(21)	169(11)	191(11)	192(11)	-15(8)	27(9)	-39(9)
C(22)	123(10)	218(11)	173(10)	27(8)	19(8)	20(8)
C(23)	175(11)	277(12)	213(11)	21(9)	29(9)	10(9)
C(24)	148(12)	420(15)	386(14)	-14(12)	11(10)	-40(11)
C(25)	135(13)	525(17)	502(16)	4(13)	75(11)	93(12)
C(26)	262(13)	354(15)	421(14)	-50(12)	72(11)	142(11)
C(27)	201(12)	284(13)	253(11)	-13(10)	29(9)	40(10)
C(28)	103(10)	173(10)	132(9)	6(8)	0(7)	-15(8)
C(29)	163(10)	154(10)	187(10)	-10(8)	-6(8)	-19(8)
C(30)	195(11)	252(12)	172(11)	81(9)	-21(9)	-41(9)
C(31)	167(11)	358(13)	127(10)	5(9)	26(8)	-47(9)
C(32)	184(11)	239(12)	197(11)	-34(9)	53(9)	23(9)
C(33)	145(10)	193(11)	172(10)	35(9)	20(8)	17(8)
O(41)	627(12)	523(12)	438(10)	41(9)	-19(9)	-318(9)

C(42A)	380(40)	550(70)	320(40)	180(40)	210(30)	80(40)
C(42B)	1090(60)	460(40)	350(30)	100(30)	230(30)	-180(40)
C(43)	542(19)	660(20)	328(14)	61(13)	88(13)	-7(15)
C(44)	337(14)	407(15)	367(13)	60(11)	105(11)	59(11)
C(45)	429(15)	324(14)	285(12)	20(11)	89(11)	11(11)

Table 6. Crystal data and structure refinement for 22 (CCDC 205423).

Empirical formula	$C_{30}H_{34}Cl_2NO_4P_2Cr \cdot CH_2Cl_2$
Formula weight	742.35
Crystallization Solvent	Dichloromethane/petroleum ether
Crystal Habit	Fragment
Crystal size	0.34 x 0.32 x 0.11 mm^3
Crystal color	Green

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 18411 reflections used in lattice determination	2.30 to 28.06°
Unit cell dimensions	a = 9.7683(6) Å b = 16.6273(10) Å β= 94.9900(10)° c = 20.9934(13) Å
Volume	3396.8(4) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/c$
Density (calculated)	1.452 Mg/m^3
F(000)	1532
Data collection program	Bruker SMART v5.054
θ range for data collection	1.56 to 28.33°
Completeness to θ = 28.33°	93.3 %
Index ranges	$-12 \le h \le 12$, $-22 \le k \le 21$, $-27 \le l \le 27$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	47756
Independent reflections	7883 [R_{int}= 0.0634]
Absorption coefficient	0.782 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9189 and 0.7769

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	7883 / 0 / 525
Treatment of hydrogen atoms	Unrestrained except for solvent
Goodness-of-fit on F^2	2.760
Final R indices [I>2σ(I), 5893 reflections]	R1 = 0.0618, *w*R2 = 0.0988
R indices (all data)	R1 = 0.0899, *w*R2 = 0.1013
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001

Average shift/error	0.000
Largest diff. peak and hole	1.796 and -1.523 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 22. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cr(1)	3660(1)	-1234(1)	2115(1)	22(1)
Cl(1)	3742(1)	-2357(1)	2752(1)	33(1)
Cl(2)	2768(1)	-1844(1)	1186(1)	30(1)
P(1)	3200(1)	134(1)	1798(1)	17(1)
P(2)	4387(1)	-225(1)	2974(1)	22(1)
O(1)	1264(2)	-951(1)	2265(1)	24(1)
O(2)	2210(2)	77(1)	459(1)	30(1)
O(3)	4629(2)	960(1)	4090(1)	28(1)
O(4)	6250(2)	-1284(1)	3639(1)	28(1)
N(1)	3859(3)	555(2)	2497(1)	19(1)
C(1)	1382(3)	319(2)	1767(1)	21(1)
C(2)	759(4)	1021(2)	1528(2)	29(1)
C(3)	-650(4)	1122(3)	1526(2)	38(1)
C(4)	-1415(4)	514(3)	1747(2)	42(1)
C(5)	-838(4)	-191(3)	1987(2)	31(1)
C(6)	574(3)	-281(2)	2006(1)	24(1)
C(7)	426(4)	-1631(2)	2420(2)	36(1)
C(8)	3868(3)	693(2)	1159(1)	19(1)
C(9)	5009(3)	1178(2)	1265(2)	23(1)
C(10)	5604(4)	1538(2)	759(2)	29(1)
C(11)	5058(4)	1398(2)	147(2)	30(1)
C(12)	3930(4)	921(2)	20(2)	30(1)
C(13)	3319(3)	565(2)	524(2)	23(1)
C(14)	1711(4)	-166(3)	-176(2)	36(1)
C(15)	3506(3)	-212(2)	3700(1)	21(1)
C(16)	2637(4)	-850(2)	3792(2)	25(1)
C(17)	1972(4)	-926(2)	4347(2)	29(1)
C(18)	2192(4)	-353(2)	4816(2)	34(1)
C(19)	3070(4)	280(2)	4747(2)	30(1)

C(20)	3739(3)	357(2)	4195(1)	23(1)
C(21)	4926(5)	1542(3)	4580(2)	33(1)
C(22)	6204(4)	11(2)	3223(1)	26(1)
C(23)	6826(3)	723(2)	3106(1)	19(1)
C(24)	8198(4)	870(2)	3275(2)	29(1)
C(25)	8985(4)	235(2)	3560(2)	32(1)
C(26)	8374(3)	-494(2)	3681(1)	22(1)
C(27)	6987(4)	-591(2)	3519(2)	26(1)
C(28)	7040(5)	-1958(3)	3843(2)	38(1)
C(29)	3459(4)	1372(2)	2697(2)	29(1)
C(30)	5663(4)	-1214(3)	1878(2)	30(1)
C(40)	156(5)	2886(3)	9454(2)	68(2)
Cl(3)	1439(1)	2790(1)	8972(1)	90(1)
Cl(4)	262(1)	2180(1)	10104(1)	57(1)

Table 8. Selected bond lengths [Å] and angles [°] for 20.

Cr(1)-C(30)	2.061(4)	C(30)-Cr(1)-Cl(1)	99.64(14)
Cr(1)-Cl(1)	2.2939(10)	C(30)-Cr(1)-Cl(2)	95.76(13)
Cr(1)-Cl(2)	2.3011(9)	Cl(1)-Cr(1)-Cl(2)	97.26(4)
Cr(1)-P(1)	2.4010(10)	C(30)-Cr(1)-P(1)	94.40(14)
Cr(1)-O(1)	2.435(2)	Cl(1)-Cr(1)-P(1)	158.22(4)
Cr(1)-P(2)	2.5204(10)	Cl(2)-Cr(1)-P(1)	97.79(3)
		C(30)-Cr(1)-O(1)	166.44(15)
		Cl(1)-Cr(1)-O(1)	93.81(6)
		Cl(2)-Cr(1)-O(1)	84.15(6)
		P(1)-Cr(1)-O(1)	72.22(6)
		C(30)-Cr(1)-P(2)	86.97(13)
		Cl(1)-Cr(1)-P(2)	97.53(3)
		Cl(2)-Cr(1)-P(2)	164.28(4)
		P(1)-Cr(1)-P(2)	66.54(3)
		O(1)-Cr(1)-P(2)	89.59(5)

Table 9. Bond lengths [Å] and angles [°] for 20.

Cr(1)-C(30)	2.061(4)	C(16)-H(16)	0.90(3)
Cr(1)-Cl(1)	2.2939(10)	C(17)-C(18)	1.374(5)
Cr(1)-Cl(2)	2.3011(9)	C(17)-H(17)	0.83(3)
Cr(1)-P(1)	2.4010(10)	C(18)-C(19)	1.373(5)
Cr(1)-O(1)	2.435(2)	C(18)-H(18)	0.93(3)
Cr(1)-P(2)	2.5204(10)	C(19)-C(20)	1.384(5)
P(1)-N(1)	1.701(2)	C(19)-H(19)	0.87(3)
P(1)-C(8)	1.799(3)	C(21)-H(21A)	0.93(4)
P(1)-C(1)	1.797(3)	C(21)-H(21B)	0.84(3)
P(2)-N(1)	1.691(3)	C(21)-H(21C)	0.96(3)
P(2)-C(15)	1.814(3)	C(22)-C(23)	1.364(4)
P(2)-C(22)	1.848(4)	C(22)-C(27)	1.375(5)
O(1)-C(6)	1.389(4)	C(23)-C(24)	1.379(5)
O(1)-C(7)	1.448(4)	C(23)-H(23)	0.90(3)
O(2)-C(13)	1.351(4)	C(24)-C(25)	1.408(5)
O(2)-C(14)	1.436(4)	C(24)-H(24)	0.88(3)
O(3)-C(20)	1.358(4)	C(25)-C(26)	1.385(5)
O(3)-C(21)	1.424(4)	C(25)-H(25)	0.99(4)
O(4)-C(27)	1.393(4)	C(26)-C(27)	1.376(5)
O(4)-C(28)	1.406(4)	C(26)-H(26)	1.05(3)
N(1)-C(29)	1.484(4)	C(28)-H(28A)	0.95(4)
C(1)-C(2)	1.391(4)	C(28)-H(28B)	0.95(5)
C(1)-C(6)	1.392(4)	C(28)-H(28C)	0.96(4)
C(2)-C(3)	1.386(5)	C(29)-H(29A)	1.05(4)
C(2)-H(2)	0.98(3)	C(29)-H(29B)	0.89(4)
C(3)-C(4)	1.363(6)	C(29)-H(29C)	0.92(3)
C(3)-H(3)	0.95(3)	C(30)-H(30A)	0.75(4)
C(4)-C(5)	1.377(6)	C(30)-H(30B)	0.87(4)
C(4)-H(4)	0.90(4)	C(30)-H(30C)	0.91(4)
C(5)-C(6)	1.384(5)	C(40)-Cl(3)	1.685(5)
C(5)-H(5)	0.96(3)	C(40)-Cl(4)	1.796(4)
C(7)-H(7A)	1.00(4)	C(40)-H(40A)	0.9965
C(7)-H(7B)	1.06(3)	C(40)-H(40B)	0.9965
C(7)-H(7C)	1.01(3)		
C(8)-C(9)	1.379(4)	C(30)-Cr(1)-Cl(1)	99.64(14)
C(8)-C(13)	1.410(4)	C(30)-Cr(1)-Cl(2)	95.76(13)
C(9)-C(10)	1.390(5)	Cl(1)-Cr(1)-Cl(2)	97.26(4)
C(9)-H(9)	0.89(3)	C(30)-Cr(1)-P(1)	94.40(14)
C(10)-C(11)	1.368(5)	Cl(1)-Cr(1)-P(1)	158.22(4)
C(10)-H(10)	0.90(3)	Cl(2)-Cr(1)-P(1)	97.79(3)
C(11)-C(12)	1.365(5)	C(30)-Cr(1)-O(1)	166.44(15)
C(11)-H(11)	0.91(3)	Cl(1)-Cr(1)-O(1)	93.81(6)
C(12)-C(13)	1.391(5)	Cl(2)-Cr(1)-O(1)	84.15(6)
C(12)-H(12)	0.91(3)	P(1)-Cr(1)-O(1)	72.22(6)
C(14)-H(14A)	1.01(4)	C(30)-Cr(1)-P(2)	86.97(13)
C(14)-H(14B)	1.00(3)	Cl(1)-Cr(1)-P(2)	97.53(3)
C(14)-H(14C)	0.99(3)	Cl(2)-Cr(1)-P(2)	164.28(4)
C(15)-C(16)	1.384(5)	P(1)-Cr(1)-P(2)	66.54(3)
C(15)-C(20)	1.410(4)	O(1)-Cr(1)-P(2)	89.59(5)
C(16)-C(17)	1.387(5)	N(1)-P(1)-C(8)	107.19(13)

N(1)-P(1)-C(1)	105.03(13)	C(9)-C(10)-H(10)	118(2)
C(8)-P(1)-C(1)	107.82(14)	C(12)-C(11)-C(10)	121.6(4)
N(1)-P(1)-Cr(1)	95.93(9)	C(12)-C(11)-H(11)	118.5(19)
C(8)-P(1)-Cr(1)	128.64(10)	C(10)-C(11)-H(11)	120(2)
C(1)-P(1)-Cr(1)	109.38(11)	C(11)-C(12)-C(13)	119.5(3)
N(1)-P(2)-C(15)	110.22(13)	C(11)-C(12)-H(12)	119(2)
N(1)-P(2)-C(22)	103.98(14)	C(13)-C(12)-H(12)	121(2)
C(15)-P(2)-C(22)	105.88(14)	O(2)-C(13)-C(12)	124.9(3)
N(1)-P(2)-Cr(1)	91.94(9)	O(2)-C(13)-C(8)	114.9(3)
C(15)-P(2)-Cr(1)	118.96(11)	C(12)-C(13)-C(8)	120.2(3)
C(22)-P(2)-Cr(1)	123.22(11)	O(2)-C(14)-H(14A)	112(2)
C(6)-O(1)-C(7)	116.7(3)	O(2)-C(14)-H(14B)	104(2)
C(6)-O(1)-Cr(1)	122.87(18)	H(14A)-C(14)-H(14B)	116(3)
C(7)-O(1)-Cr(1)	116.6(2)	O(2)-C(14)-H(14C)	109.6(15)
C(13)-O(2)-C(14)	117.9(3)	H(14A)-C(14)-H(14C)	105(3)
C(20)-O(3)-C(21)	118.5(3)	H(14B)-C(14)-H(14C)	111(3)
C(27)-O(4)-C(28)	115.8(3)	C(16)-C(15)-C(20)	118.2(3)
C(29)-N(1)-P(2)	127.5(2)	C(16)-C(15)-P(2)	116.8(2)
C(29)-N(1)-P(1)	122.1(2)	C(20)-C(15)-P(2)	124.8(3)
P(2)-N(1)-P(1)	105.58(14)	C(15)-C(16)-C(17)	121.7(3)
C(2)-C(1)-C(6)	119.2(3)	C(15)-C(16)-H(16)	120.0(19)
C(2)-C(1)-P(1)	123.8(3)	C(17)-C(16)-H(16)	118.3(19)
C(6)-C(1)-P(1)	117.0(2)	C(18)-C(17)-C(16)	118.9(4)
C(3)-C(2)-C(1)	120.4(4)	C(18)-C(17)-H(17)	119(2)
C(3)-C(2)-H(2)	121.3(18)	C(16)-C(17)-H(17)	122(2)
C(1)-C(2)-H(2)	118.2(18)	C(19)-C(18)-C(17)	121.0(3)
C(4)-C(3)-C(2)	118.8(4)	C(19)-C(18)-H(18)	120.4(19)
C(4)-C(3)-H(3)	123(2)	C(17)-C(18)-H(18)	118.2(19)
C(2)-C(3)-H(3)	118(2)	C(18)-C(19)-C(20)	120.3(3)
C(3)-C(4)-C(5)	122.5(4)	C(18)-C(19)-H(19)	117(2)
C(3)-C(4)-H(4)	124(2)	C(20)-C(19)-H(19)	123(2)
C(5)-C(4)-H(4)	113(2)	O(3)-C(20)-C(19)	124.1(3)
C(4)-C(5)-C(6)	118.6(4)	O(3)-C(20)-C(15)	116.1(3)
C(4)-C(5)-H(5)	120(2)	C(19)-C(20)-C(15)	119.9(3)
C(6)-C(5)-H(5)	121(2)	O(3)-C(21)-H(21A)	110(2)
C(5)-C(6)-O(1)	123.1(3)	O(3)-C(21)-H(21B)	105(2)
C(5)-C(6)-C(1)	120.5(3)	H(21A)-C(21)-H(21B)	106(3)
O(1)-C(6)-C(1)	116.4(3)	O(3)-C(21)-H(21C)	111.4(17)
O(1)-C(7)-H(7A)	110(2)	H(21A)-C(21)-H(21C)	109(3)
O(1)-C(7)-H(7B)	108.6(18)	H(21B)-C(21)-H(21C)	114(3)
H(7A)-C(7)-H(7B)	115(3)	C(23)-C(22)-C(27)	118.4(3)
O(1)-C(7)-H(7C)	105.6(18)	C(23)-C(22)-P(2)	124.4(3)
H(7A)-C(7)-H(7C)	107(3)	C(27)-C(22)-P(2)	117.2(3)
H(7B)-C(7)-H(7C)	111(3)	C(22)-C(23)-C(24)	123.1(3)
C(9)-C(8)-C(13)	118.4(3)	C(22)-C(23)-H(23)	125(2)
C(9)-C(8)-P(1)	121.5(2)	C(24)-C(23)-H(23)	111.8(19)
C(13)-C(8)-P(1)	119.6(2)	C(23)-C(24)-C(25)	117.4(4)
C(8)-C(9)-C(10)	121.0(3)	C(23)-C(24)-H(24)	117(2)
C(8)-C(9)-H(9)	120.0(18)	C(25)-C(24)-H(24)	126(2)
C(10)-C(9)-H(9)	119.0(18)	C(26)-C(25)-C(24)	120.4(3)
C(11)-C(10)-C(9)	119.4(4)	C(26)-C(25)-H(25)	121(2)
C(11)-C(10)-H(10)	122(2)	C(24)-C(25)-H(25)	119(2)

C(27)-C(26)-C(25)	119.2(3)	N(1)-C(29)-H(29C)	109(2)
C(27)-C(26)-H(26)	107.0(15)	H(29A)-C(29)-H(29C)	107(3)
C(25)-C(26)-H(26)	133.7(15)	H(29B)-C(29)-H(29C)	110(3)
C(26)-C(27)-C(22)	121.5(3)	Cr(1)-C(30)-H(30A)	108(3)
C(26)-C(27)-O(4)	124.5(3)	Cr(1)-C(30)-H(30B)	114(2)
C(22)-C(27)-O(4)	114.1(3)	H(30A)-C(30)-H(30B)	112(4)
O(4)-C(28)-H(28A)	109(2)	Cr(1)-C(30)-H(30C)	106(2)
O(4)-C(28)-H(28B)	106(3)	H(30A)-C(30)-H(30C)	102(3)
H(28A)-C(28)-H(28B)	107(4)	H(30B)-C(30)-H(30C)	114(3)
O(4)-C(28)-H(28C)	113(2)	Cl(3)-C(40)-Cl(4)	113.4(3)
H(28A)-C(28)-H(28C)	111(3)	Cl(3)-C(40)-H(40A)	108.9
H(28B)-C(28)-H(28C)	111(4)	Cl(4)-C(40)-H(40A)	108.9
N(1)-C(29)-H(29A)	113.0(19)	Cl(3)-C(40)-H(40B)	108.9
N(1)-C(29)-H(29B)	108(3)	Cl(4)-C(40)-H(40B)	108.9
H(29A)-C(29)-H(29B)	110(3)	H(40A)-C(40)-H(40B)	107.7

Table 10. Anisotropic displacement parameters ($Å^2 x 10^4$) for 20. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr(1)	270(3)	220(3)	169(3)	-1(2)	43(2)	27(2)
Cl(1)	492(6)	225(5)	284(5)	15(4)	63(4)	42(4)
Cl(2)	341(5)	339(5)	225(4)	-68(4)	65(4)	-46(4)
P(1)	157(4)	225(4)	135(4)	4(3)	-2(3)	4(4)
P(2)	220(5)	284(5)	140(4)	15(4)	11(3)	50(4)
O(1)	228(12)	275(13)	225(12)	1(10)	52(10)	-54(10)
O(2)	342(14)	388(15)	165(11)	-40(10)	-41(10)	-50(12)
O(3)	292(14)	350(14)	211(12)	-38(10)	37(10)	-65(11)
O(4)	270(13)	238(13)	321(13)	70(10)	1(11)	11(11)
N(1)	211(15)	205(14)	137(13)	-4(11)	6(11)	-15(11)
C(1)	183(17)	291(19)	157(15)	-26(14)	7(13)	36(14)
C(2)	250(20)	410(20)	223(18)	34(16)	6(16)	70(17)
C(3)	380(20)	480(30)	280(20)	19(18)	-19(18)	190(20)
C(4)	210(20)	880(40)	161(18)	-30(20)	-1(16)	100(20)
C(5)	207(19)	570(30)	159(17)	-74(17)	14(14)	-47(19)
C(6)	200(18)	380(20)	128(15)	-64(14)	-14(13)	-21(15)
C(7)	320(20)	370(20)	410(20)	-29(19)	130(20)	-122(19)
C(8)	211(18)	205(18)	170(16)	16(13)	41(13)	43(14)
C(9)	209(18)	269(19)	206(18)	10(15)	-2(14)	42(15)
C(10)	220(20)	260(20)	390(20)	23(16)	97(17)	21(16)
C(11)	320(20)	340(20)	260(20)	119(16)	120(17)	87(17)
C(12)	360(20)	360(20)	167(18)	27(15)	15(16)	96(17)
C(13)	252(19)	252(18)	180(16)	11(14)	13(14)	47(15)
C(14)	370(20)	490(30)	220(19)	-120(19)	-36(17)	80(20)
C(15)	222(18)	260(18)	162(16)	17(14)	21(13)	67(15)
C(16)	290(20)	290(20)	157(17)	-26(15)	2(14)	37(16)
C(17)	350(20)	310(20)	213(18)	28(16)	47(16)	-94(18)
C(18)	420(20)	430(20)	183(18)	5(16)	137(17)	-19(18)

C(19)	370(20)	350(20)	186(18)	-61(16)	59(16)	-36(17)
C(20)	225(19)	294(19)	156(16)	-4(14)	-8(14)	22(15)
C(21)	320(20)	410(30)	250(20)	-39(18)	20(18)	-90(20)
C(22)	330(20)	300(20)	133(16)	-28(14)	35(14)	7(16)
C(23)	209(18)	208(18)	148(16)	10(13)	8(13)	-10(14)
C(24)	320(20)	350(20)	201(18)	-21(16)	30(16)	-96(18)
C(25)	280(20)	460(20)	231(18)	-58(17)	17(16)	-35(18)
C(26)	250(20)	235(19)	162(16)	-30(14)	9(14)	13(15)
C(27)	270(20)	320(20)	200(17)	-61(15)	48(15)	11(16)
C(28)	340(20)	360(30)	420(30)	30(20)	0(20)	90(20)
C(29)	370(20)	270(20)	230(20)	-24(17)	38(18)	-40(17)
C(30)	300(20)	350(30)	250(20)	-10(20)	57(18)	87(19)
C(40)	660(30)	990(40)	370(30)	190(20)	-70(20)	190(30)
Cl(3)	566(8)	1552(14)	586(8)	-149(9)	61(7)	-426(9)
Cl(4)	697(8)	578(7)	399(6)	97(5)	-204(6)	-175(6)

Table 11. Crystal data and structure refinement for 22.

Empirical formula	$C_{29}H_{31}NO_4P_2I_3Cr \cdot CH_2Cl_2$
Formula weight	1037.11
Crystallization Solvent	Dichloromethane
Crystal Habit	Block
Crystal size	0.29 x 0.22 x 0.21 mm^3
Crystal color	Dark brown

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 39991 reflections used in lattice determination	2.18 to 34.78°
Unit cell dimensions	a = 13.5277(3) Å b = 13.5151(3) Å β= 107.8920(10)° c = 20.3801(5) Å
Volume	3545.85(14) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.943 Mg/m^3
F(000)	1996
Data collection program	Bruker SMART v5.054
θ range for data collection	1.61 to 35.00°
Completeness to θ = 35.00°	92.6 %
Index ranges	$-21 \le h \le 21$, $-21 \le k \le 19$, $-32 \le l \le 32$
Data collection scan type	ω scans at 3 ϕ settings each for 2 2θ values and 1 ϕ scan
Data reduction program	Bruker SAINT v6.022
Reflections collected	84909
Independent reflections	14452 [R_{int}= 0.0606]
Absorption coefficient	3.211 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.5520 and 0.4562

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Patterson method
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	14452 / 0 / 393
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.405
Final R indices [I>2σ(I), 10704 reflections]	R1 = 0.0335, *w*R2 = 0.0499
R indices (all data)	R1 = 0.0533, *w*R2 = 0.0516
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$

Max shift/error	0.006
Average shift/error	0.000
Largest diff. peak and hole	2.408 and -1.597 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 22. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cr	6003(1)	8480(1)	7573(1)	10(1)
I(1)	7423(1)	8550(1)	6915(1)	18(1)
I(2)	7310(1)	8642(1)	8855(1)	15(1)
I(3)	5567(1)	10392(1)	7425(1)	17(1)
P(1)	4506(1)	8200(1)	6600(1)	11(1)
P(2)	4409(1)	8032(1)	7902(1)	11(1)
O(1)	6012(1)	6883(1)	7419(1)	12(1)
O(2)	4707(1)	8437(1)	5161(1)	21(1)
O(3)	2329(1)	7855(1)	8166(1)	22(1)
O(4)	5330(1)	7329(1)	9299(1)	17(1)
N	3663(1)	8037(1)	7060(1)	11(1)
C(1)	4724(2)	6982(2)	6314(1)	11(1)
C(2)	4154(2)	6549(2)	5692(1)	14(1)
C(3)	4358(2)	5583(2)	5547(1)	17(1)
C(4)	5124(2)	5054(2)	6017(1)	18(1)
C(5)	5710(2)	5462(2)	6645(1)	14(1)
C(6)	5493(2)	6428(2)	6790(1)	13(1)
C(7)	6717(2)	6241(2)	7931(1)	18(1)
C(8)	3810(2)	8999(2)	5895(1)	19(1)
C(9)	3100(2)	9691(2)	6048(1)	15(1)
C(10)	2573(2)	10353(2)	5557(1)	23(1)
C(11)	2727(2)	10357(2)	4908(1)	26(1)
C(12)	3413(2)	9717(2)	4757(1)	23(1)
C(13)	3976(2)	9050(2)	5252(1)	21(1)
C(14)	4783(2)	8379(2)	4469(1)	29(1)
C(15)	3847(2)	8809(2)	8417(1)	13(1)
C(16)	4448(2)	9594(2)	8772(1)	17(1)

C(17)	4091(2)	10216(2)	9190(1)	20(1)
C(18)	3121(2)	10059(2)	9255(1)	19(1)
C(19)	2504(2)	9283(2)	8910(1)	18(1)
C(20)	2872(2)	8651(2)	8504(1)	14(1)
C(21)	1392(2)	7588(2)	8315(1)	33(1)
C(22)	4394(2)	6766(2)	8201(1)	13(1)
C(23)	3992(2)	5981(2)	7752(1)	17(1)
C(24)	4117(2)	5009(2)	7974(1)	23(1)
C(25)	4682(2)	4798(2)	8648(1)	24(1)
C(26)	5095(2)	5559(2)	9113(1)	21(1)
C(27)	4946(2)	6533(2)	8891(1)	14(1)
C(28)	6083(2)	7145(2)	9950(1)	21(1)
C(29)	2585(2)	7686(2)	6747(1)	17(1)
C(31)	8092(2)	6545(2)	5770(1)	27(1)
Cl(1)	8834(1)	7295(1)	5380(1)	39(1)
Cl(2)	6755(1)	6703(1)	5365(1)	28(1)

Table 13. Selected bond lengths [Å] and angles [°] for 22.

Cr-O(1)	2.1820(14)	O(1)-Cr-P(1)	76.39(4)
Cr-P(1)	2.3891(6)	O(1)-Cr-P(2)	81.06(4)
Cr-P(2)	2.5205(6)	P(1)-Cr-P(2)	66.825(18)
Cr-I(3)	2.6481(3)	O(1)-Cr-I(3)	163.77(4)
Cr-I(1)	2.6604(3)	P(1)-Cr-I(3)	87.552(16)
Cr-I(2)	2.6765(3)	P(2)-Cr-I(3)	94.931(16)
		O(1)-Cr-I(1)	85.70(4)
		P(1)-Cr-I(1)	98.403(16)
		P(2)-Cr-I(1)	162.091(17)
		I(3)-Cr-I(1)	94.446(11)
		O(1)-Cr-I(2)	100.99(3)
		P(1)-Cr-I(2)	163.862(18)
		P(2)-Cr-I(2)	97.064(15)
		I(3)-Cr-I(2)	95.099(10)
		I(1)-Cr-I(2)	97.260(11)

Table 14. Bond lengths [Å] and angles [°] for 22.

Cr-O(1)	2.1820(14)	P(2)-N	1.7020(16)
Cr-P(1)	2.3891(6)	P(2)-C(15)	1.808(2)
Cr-P(2)	2.5205(6)	P(2)-C(22)	1.819(2)
Cr-I(3)	2.6481(3)	O(1)-C(6)	1.400(2)
Cr-I(1)	2.6604(3)	O(1)-C(7)	1.462(2)
Cr-I(2)	2.6765(3)	O(2)-C(13)	1.347(3)
P(1)-N	1.6990(16)	O(2)-C(14)	1.448(2)
P(1)-C(1)	1.800(2)	O(3)-C(20)	1.364(2)
P(1)-C(8)	1.813(2)	O(3)-C(21)	1.436(3)

O(4)-C(27)	1.362(2)	N-P(2)-C(22)	106.10(9)
O(4)-C(28)	1.424(2)	C(15)-P(2)-C(22)	107.58(9)
N-C(29)	1.478(3)	N-P(2)-Cr	91.26(6)
C(1)-C(2)	1.394(3)	C(15)-P(2)-Cr	124.14(7)
C(1)-C(6)	1.400(3)	C(22)-P(2)-Cr	114.39(7)
C(2)-C(3)	1.385(3)	C(6)-O(1)-C(7)	115.33(14)
C(3)-C(4)	1.377(3)	C(6)-O(1)-Cr	122.86(11)
C(4)-C(5)	1.396(3)	C(7)-O(1)-Cr	120.95(11)
C(5)-C(6)	1.389(3)	C(13)-O(2)-C(14)	116.30(17)
C(8)-C(13)	1.396(3)	C(20)-O(3)-C(21)	117.71(16)
C(8)-C(9)	1.442(3)	C(27)-O(4)-C(28)	117.43(16)
C(9)-C(10)	1.368(3)	C(29)-N-P(1)	122.88(12)
C(10)-C(11)	1.401(3)	C(29)-N-P(2)	129.43(13)
C(11)-C(12)	1.371(3)	P(1)-N-P(2)	105.42(9)
C(12)-C(13)	1.393(3)	C(2)-C(1)-C(6)	119.35(18)
C(15)-C(16)	1.396(3)	C(2)-C(1)-P(1)	125.32(16)
C(15)-C(20)	1.400(3)	C(6)-C(1)-P(1)	115.20(14)
C(16)-C(17)	1.384(3)	C(3)-C(2)-C(1)	119.99(19)
C(17)-C(18)	1.375(3)	C(4)-C(3)-C(2)	119.81(19)
C(18)-C(19)	1.389(3)	C(3)-C(4)-C(5)	121.82(19)
C(19)-C(20)	1.385(3)	C(6)-C(5)-C(4)	117.92(19)
C(22)-C(23)	1.398(3)	C(5)-C(6)-O(1)	121.78(17)
C(22)-C(27)	1.409(3)	C(5)-C(6)-C(1)	121.09(18)
C(23)-C(24)	1.383(3)	O(1)-C(6)-C(1)	117.11(17)
C(24)-C(25)	1.380(3)	C(13)-C(8)-C(9)	118.68(19)
C(25)-C(26)	1.393(3)	C(13)-C(8)-P(1)	125.42(18)
C(26)-C(27)	1.388(3)	C(9)-C(8)-P(1)	115.64(15)
C(31)-Cl(2)	1.755(2)	C(10)-C(9)-C(8)	119.94(19)
C(31)-Cl(1)	1.776(2)	C(9)-C(10)-C(11)	119.8(2)
		C(12)-C(11)-C(10)	121.2(2)
O(1)-Cr-P(1)	76.39(4)	C(11)-C(12)-C(13)	120.2(2)
O(1)-Cr-P(2)	81.06(4)	O(2)-C(13)-C(12)	124.0(2)
P(1)-Cr-P(2)	66.825(18)	O(2)-C(13)-C(8)	115.80(19)
O(1)-Cr-I(3)	163.77(4)	C(12)-C(13)-C(8)	120.2(2)
P(1)-Cr-I(3)	87.552(16)	C(16)-C(15)-C(20)	118.10(18)
P(2)-Cr-I(3)	94.931(16)	C(16)-C(15)-P(2)	117.43(15)
O(1)-Cr-I(1)	85.70(4)	C(20)-C(15)-P(2)	124.41(15)
P(1)-Cr-I(1)	98.403(16)	C(17)-C(16)-C(15)	121.57(19)
P(2)-Cr-I(1)	162.091(17)	C(18)-C(17)-C(16)	119.2(2)
I(3)-Cr-I(1)	94.446(11)	C(17)-C(18)-C(19)	120.79(19)
O(1)-Cr-I(2)	100.99(3)	C(20)-C(19)-C(18)	119.77(19)
P(1)-Cr-I(2)	163.862(18)	O(3)-C(20)-C(19)	123.45(18)
P(2)-Cr-I(2)	97.064(15)	O(3)-C(20)-C(15)	116.04(17)
I(3)-Cr-I(2)	95.099(10)	C(19)-C(20)-C(15)	120.51(19)
I(1)-Cr-I(2)	97.260(11)	C(23)-C(22)-C(27)	117.61(18)
N-P(1)-C(1)	105.33(9)	C(23)-C(22)-P(2)	122.48(15)
N-P(1)-C(8)	104.00(9)	C(27)-C(22)-P(2)	119.17(15)
C(1)-P(1)-C(8)	112.59(9)	C(24)-C(23)-C(22)	121.58(19)
N-P(1)-Cr	95.97(6)	C(25)-C(24)-C(23)	119.7(2)
C(1)-P(1)-Cr	103.40(7)	C(24)-C(25)-C(26)	120.6(2)
C(8)-P(1)-Cr	131.72(7)	C(27)-C(26)-C(25)	119.35(19)
N-P(2)-C(15)	110.96(9)	O(4)-C(27)-C(26)	124.07(18)

O(4)-C(27)-C(22)	114.78(17)
C(26)-C(27)-C(22)	121.13(19)
Cl(2)-C(31)-Cl(1)	111.27(13)

Table 15. Anisotropic displacement parameters ($Å^2 x 10^4$) for 22. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr	97(2)	105(2)	89(1)	-2(1)	18(1)	1(1)
I(1)	210(1)	186(1)	180(1)	-39(1)	119(1)	-52(1)
I(2)	130(1)	186(1)	104(1)	-11(1)	2(1)	-8(1)
I(3)	189(1)	110(1)	181(1)	5(1)	30(1)	11(1)
P(1)	117(3)	108(3)	85(2)	5(2)	20(2)	0(2)
P(2)	105(3)	119(3)	92(2)	-5(2)	23(2)	5(2)
O(1)	153(7)	101(7)	85(6)	4(5)	7(5)	26(6)
O(2)	219(8)	218(8)	199(7)	34(6)	94(6)	39(7)
O(3)	187(8)	230(9)	286(8)	-95(7)	133(7)	-96(7)
O(4)	175(8)	186(8)	123(7)	12(6)	-2(6)	12(6)
N	90(8)	144(9)	98(7)	-1(6)	18(6)	6(7)
C(1)	118(10)	128(10)	110(9)	0(7)	53(7)	-21(8)
C(2)	130(10)	188(11)	119(9)	-6(8)	47(7)	-18(8)
C(3)	184(11)	204(11)	148(10)	-79(8)	77(8)	-68(9)
C(4)	171(11)	155(11)	240(11)	-68(8)	120(9)	-32(9)
C(5)	148(10)	126(10)	146(9)	2(7)	67(8)	4(8)
C(6)	106(10)	150(10)	136(9)	-22(7)	60(7)	-22(8)
C(7)	199(12)	137(11)	141(10)	11(7)	-18(8)	64(8)
C(8)	189(12)	179(11)	151(10)	20(8)	-3(8)	-52(9)
C(9)	143(10)	133(10)	149(10)	20(7)	17(8)	-6(8)
C(10)	190(12)	196(12)	282(12)	41(9)	36(9)	20(9)
C(11)	243(13)	238(13)	244(12)	76(9)	-1(9)	-33(10)
C(12)	204(12)	235(12)	200(11)	98(9)	-32(9)	-41(10)
C(13)	180(12)	190(11)	238(11)	-4(9)	47(9)	-15(9)
C(14)	338(14)	365(15)	190(11)	15(10)	119(10)	-27(11)
C(15)	137(10)	137(10)	103(9)	1(7)	37(7)	7(8)
C(16)	155(11)	204(11)	171(10)	-46(8)	74(8)	-18(9)
C(17)	218(12)	187(11)	199(10)	-67(8)	70(9)	-15(9)
C(18)	212(12)	190(11)	193(11)	-12(8)	109(9)	42(9)
C(19)	158(11)	203(11)	213(11)	16(8)	108(9)	14(9)
C(20)	150(10)	142(10)	144(9)	11(8)	53(8)	-31(8)
C(21)	261(14)	322(15)	474(15)	-110(12)	221(12)	-165(11)
C(22)	119(10)	143(10)	139(9)	16(7)	49(8)	14(8)
C(23)	184(11)	181(11)	143(10)	-10(8)	40(8)	-38(9)
C(24)	279(13)	149(11)	221(11)	-8(8)	41(9)	-60(10)
C(25)	271(13)	148(11)	292(12)	71(9)	75(10)	-23(9)
C(26)	208(12)	231(12)	176(10)	70(8)	49(9)	-3(9)
C(27)	115(10)	177(11)	142(9)	6(8)	47(7)	-14(8)
C(28)	192(12)	272(13)	114(10)	16(8)	-30(8)	-5(9)
C(29)	109(10)	230(12)	145(10)	-37(8)	14(8)	-8(8)
C(31)	281(14)	213(13)	299(12)	46(9)	63(10)	51(10)
Cl(1)	267(3)	293(4)	641(4)	12(3)	185(3)	-16(3)
Cl(2)	248(3)	315(3)	310(3)	-68(2)	120(2)	-38(3)

Figure 1. Drawing of **21**. The quality of the dataset precluded reliable determination of structural parameters.

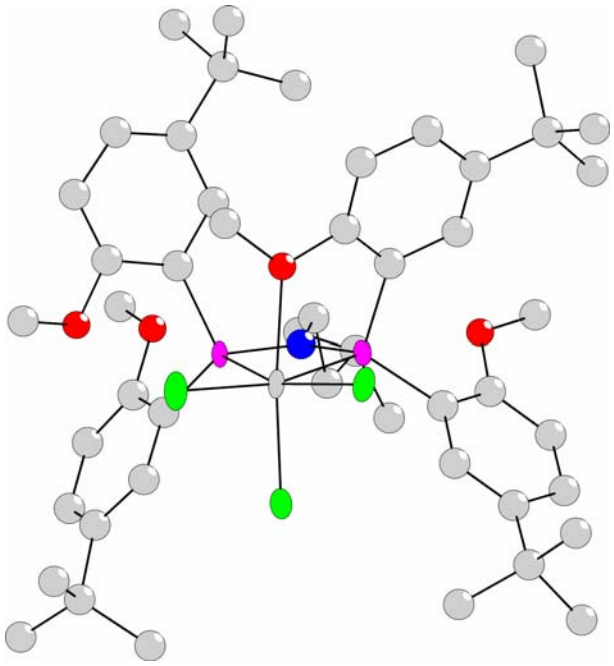

Figure 2. Plot of ethylene consumption over time for **18**, **21**, and **23** activated with MAO.